AD-A235 857

REPORT DOCUMEN

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT for unlimited distribution and release
2b. DECLASSIFICATION DOWNGRADING SCHEDULE		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 1148-12		5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Lowell	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research-Chemistry Division
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry-One University Avenue Lowell, Massachusetts 01854		7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, Virginia 22217-5000
8a. NAME OF FUNDING-SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1148

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

Second Harmonic Properties of Aromatic Schiff's Bases Functionalized in the Side Chains of Polymethylmethacrylate

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT Technical	13b. TIME COVERED From 900601 To 910531	14. DATE OF REPORT (Year, Month, Day) 910503	15. PAGE COUNT eight (8)

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Polymeric thin films doped with NLO molecules are easily prepared. Recently, we have reported a number of new homo- and co- polymers in which the NLO molecules separated by flexible methylene spacer are covalently attached in the side chain of polymethacrylate (PMA) backbone. Aromatic Schiff's bases substituted with appropriate donor acceptor groups have been chosen because of their high ground-state dipole moment and large molecular hyperpolarizability. In this report, the synthesis, characterization, non-linear optical properties and preparation and characterization of mono or multilayer films of new side chain polymers are presented and discussed.

20. DISTRIBUTION AVAILABILITY OF ABSTRACT x) UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD Form 1473, JUN 86 *Previous editions are obsolete* SECURITY CLASSIFICATION OF THIS PAGE

OFFICE OF NAVAL RESEARCH

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to be published in

Proceedings of International Symposium on Non Linear Optical Materials
University of Texas at El Paso
October 28 - November 2, 1990

University of Lowell
Department of Chemistry
Lowell, Massachusetts

May 3, 1991

91 5 23 011

91-00404

SECOND HARMONIC PROPERTIES OF AROMATIC SCHIFF'S BASES FUNCTIONALIZED IN THE SIDE CHAINS OF POLYMETHYLMETHACRYLATE

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Introduction

During the past decade, the nonlinear optical (NLO) properties of organic materials have been extensively investigated. It has been established that the delocalized π-electronic systems of acentric aromatic molecules can lead to higher second order NLO coefficients than those of traditional inorganic materials. A number of potential applications, viz. second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric amplification and oscillation have been proposed. The major opportunity associated with the organic materials is the design and synthesis of dipolar molecules with noncentrosymmetric structure and large molecular hyperpolarizability. This is a prerequisite for second order optical effects. In addition, noncentrosymmetric alignment of the molecules on the macroscopic level is essentially necessary.

Polymeric thin films doped with NLO molecules are easily prepared. However, the limited solubility of NLO active molecules in a host polymeric matrix and the fast relaxation of second order properties of poled polymeric films are the major disadvantages. Side chain polymers have attracted attention since a large number of NLO molecules can be covalently attached to the polymer chain and hence possess higher optical nonlinearities with slow relaxation compared to doped polymer systems[1,2].

Recently, we have reported a number of new homo- and co-polymers in which the NLO molecules separated by flexible methylene spacer are covalently attached in the side chain of polymethacrylate (PMA) backbone. Aromatic Schiff's bases substituted with appropriate donor acceptor groups have been chosen because of their high ground-state dipole moment and large molecular hyperpolarizability[3].

The Langmuir-Blodgett (LB) technique is capable of producing high quality, oriented films of organic materials. The close control of layer

thickness and molecular orientation makes this technique particularly attractive for application of NLO molecules[4]. In this way, the alignment of the NLO moieties can be expected to be achieved without the poling procedure. In this report, the synthesis, characterization, non-linear optical properties and preparation and characterization of mono or multilayer films of new side chain polymers are presented and discussed.

Experimental

Polymer Synthesis

In a four-step procedure, Schiff's bases, substituted with acceptor and donor groups in para positions, were prepared by the condensation of amine and aldehyde. Hydroxy-terminated octamethylene spacer was attached by reacting the mono-sodium salt of Schiff's base with 1-bromooctanol. Esterfication with methacryloylchloride produced the desired monomer. Homo- and copolymer were synthesized from corresponding methacrylate monomers by radical polymerization(Fig.1). The synthesis of these molecules has been reported in our earlier communication[5].

Processing and Poling

Polymers were dissolved in 1,4-dioxane (about 10% wt/vol) and filtered through 0.5 μm membrane filter and then spin coated on the glass plates at 2000-4000 rpm. The corona poling technique was used to align the NLO molecules[6]. The poling temperature was close to T_g of copolymer 2(Tab.1.). The poling voltage on the corona wire was maintained at 5.5 kV while a corona current of approximately 1.6 μA was established. The poling field was kept on during both the heating and the cooling cycles.

NLO measurements

Measurements were made on a Q-switched Nd:YAG laser (Quantel 660A) in which a polarized beam of 1064 nm wavelength was passed through the sample. The fundamental wave was blocked using $CuSO_4$ solution and a 532 nm interference filter was used to allow the second harmonic wavelength to pass. The SH signal was detected by a photomultiplier tube (PMT) then amplified and averaged in a boxcar integrator.

Preparation of LB Films

The LB equipment used in this work included both Lauda MGW film balance and a moving wall method LB film deposition apparatus (Nippon Laser & Electronics (NL-LB-240-MWC))[7]. The moving wall apparatus consisted of a Teflon trough, two teflon barriers (one is fixed and the other is moveable) and teflon coated moving (side) walls. The width of the moving wall is the same as that of the substrate (50 mm) to prevent shear flow of the monolayer during deposition. The moving wall is designed to move simultaneously with the moving barrier during compression and deposition to prevent friction between the monolayer edges and wall. The surface pressure of the monolayer is continuously monitored using the Wilhelmy plate method.

Polymers were dissolved in chloroform to a concentration of approximately 0.6 mg/ml, and filtered through a 1 μm membrane filter and spread onto either pure water or 2×10^{-4} M $CdCl_2$ subphases. A Millipore Milli-Q system was used for subphase preparation and a constant temperature bath was used to control the subphase temperature (20°C). Mono- and multilayer films were transfered onto hydrophilic glass substrates using the vertical deposition technique. Multilayers were obtained by repeating the procedure.

Result and Discussion

Polymer Characterization

All polymers have been characterized by elemental analyses, GPC, ^{1}H-NMR, DSC, TGA, IR and UV. Physical properties of the polymers are listed in Tab.1. The molecular weight of the homopolymers were very low as indicated by the GPC. Two copolymers have been synthesized from the following two standpoints. One is to obtain high molecular weight polymer in which the movement of side chains is more efficiently restricted compared with low molecular weight polymer. The other is to increase the flexibility of the polymer backbone to optimize the deposition of mono- or multilayered LB films. High molecular weight product was obtained as the proportion of methylmethacrylate (MMA) was increased. Copolymers were synthesized by copolymerization of MMA and M5C8MA (Fig.1.) using 5 : 1 and 18 : 1 ratio. Elemental analyses indicate that the ratio between the MMA and M5C8MA segments is 2.5 in copolymer 1 and 9.5 in copolymer 2.

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Polymers showed the visible absorption cut-off wavelength well before the wavelength of SH frequency at 532 nm. Lower T_g values compared to PMMA (T_g = 104 °C) were observed in all cases due to the internal plasticizing effect arising from the flexible octamethylene spacer group in the side chain.

SHG Properties

The NLO coefficient d_{33} of copolymer 2 was obtained by comparing the SHG intensity of copolymer 2 with the SHG intensity of fused quartz (d_{11} coefficient) as the reference material. The d_{33} for copolymer 2 was found to be about 3 pm/V at 1064 nm. In general, the aligned NLO molecules exhibit slow relaxation when the poling field is withdrawn. The retention of the SHG intensity of copolymer 2 was found to be better than the guest host systems (Fig.2). This is due to the fact that NLO molecules are linked covalently in the side chains of the PMA backbone. The movement of NLO molecules are restricted relatively. The detailed linear and nonlinear optical properties of copolymer 2 will be published elsewhere[8].

Characterization of LB Films

It was extremely difficult to achieve complete vertical transfer onto glass substrates using the Lauda Film Balance. Typically transfer ratio of only 20-30 % were achieved on each pass. It is believed that this difficulty is due to the extreme rigidity of the polymeric monolayer film. Therefore, monolayer characterization and transfer were pursued on the Nippon Laser & Electronics(NLE) trough using the moving wall method.

The pressure-area isotherm of PM5C8MA is shown in Fig.3. It indicates the molecules begin to pack into the expanded state at an area per molecules of approximately 65 Å^2 per monomer unit. As compression continues, a long plateau region occurs at relatively low surface pressure. The isotherm then becomes steeper with a limiting molecular area of about 35 Å^2 and a collapse pressure of 20 mN/m. This behavior suggests that at low surface pressure the polar group of the polymer side chains are lying flat on the subphase surface, with the hydrocarbon backbone protruding away from the surface. At higher pressure the polar side groups are packed more tightly and are oriented. However, we feel contrary to early reported results[9,10] the polar groups for this system are inclined to the plane of the film at a very shallow angle.

Mono-and multilayer films could be easily transfered onto the glass substrates using the vertical deposition technique using the NLE trough.

Transfer ratios of about 1.0 (upstroke) and 0.95 (downstroke) were obtained on each pass. This improvement in transfer is believed to be due to a minimization of shear flow using the moving wall method.

Fig.4. shows the polarized UV-visible spectra at 45° incidence of a multilayer (11 layers) of PM5C8MA. The absorbance of the p-polarized spectrum is weak in comparison with that of the s-polarized spectrum. Similar behavior was observed for PM2C8MA and copolymers. Detailed data analysis indicates that the polar group (NLO molecules) in the side chain is lying in an orientation of about 30° to the substrate surface[11,12]. The SHG signal from a monolayer only 30 Å thick is readly observable. The effective 'd' co-efficients, however, have not been calculated but are expected to be significant for this homopolymer.

Stearic acid is well known to have an ideal molecular orientation in LB films. Mixed monolayers of Stearic Acid and PM5C8MA were prepared in an attempt to optimize the orientation of the NLO molecules in the polymer. Fig.3. shows the pressure-area isotherm of PM5C8MA and stearic acid by using a mole ratio of 4 : 1. The curve is steeper when compared to that of PM5C8MA. The orientation of the NLO component is expected to be improved and hence further enhancement of the 'd' coefficient is expected. Further characterization studies regarding the orientation of the polar group in the side chain is in progress.
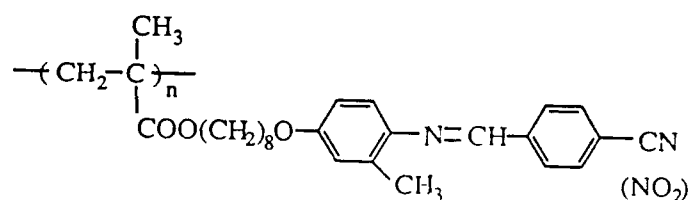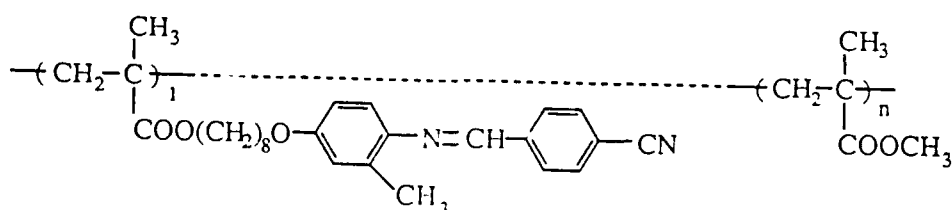
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PM5C8MA (PM2C8MA)

copolymer (n = 9.5 , 2.5)

Fig. 1. Structure of homo- and copoymers

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Tab. 1. Physical properties of homo- and copolymers

Polymer	$\overline{M_w}$ a)	$T_g/°C$ b)	PDT/°C c)	$\lambda_{max}(nm)$ d)
PM2C8MA	5000	6 6	2 4 0	3 8 5
PM5C8MA	4400	5 2	2 8 5	3 6 5
Coplymer 1 (n = 2.5)	17700	7 8	2 7 5	3 6 5
Coplymer 2 (n = 9.5)	86700	8 9	2 6 6	3 6 5

a) Molecular weight was determined by GPC. Measurements were done in THF using polystyrene standard as reference.
b) T_g was determined by DSC.
c) PDT was determined from TGA curve.
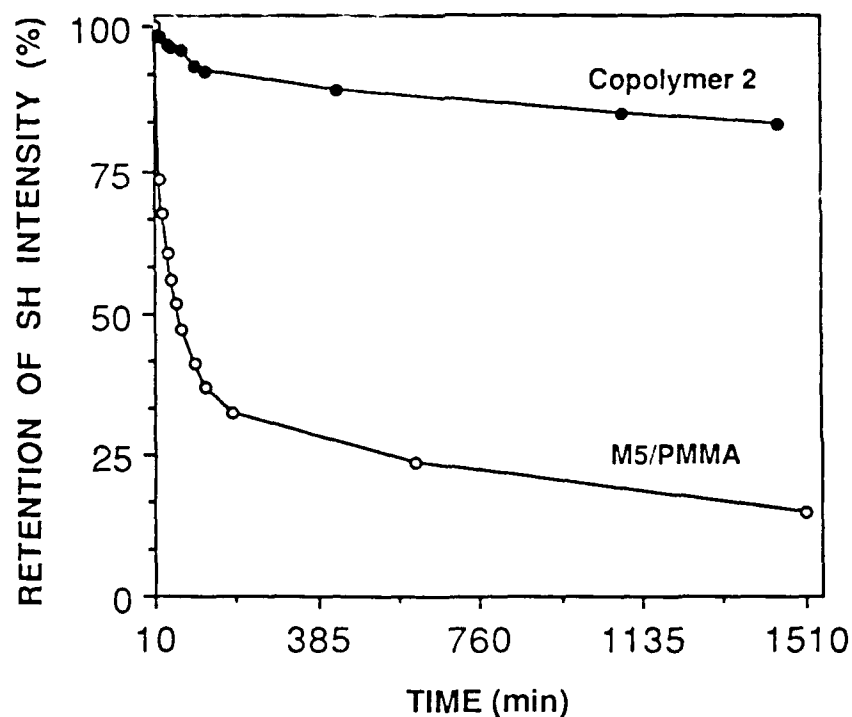d) UV-visible absorption was measued in chloroform solution.

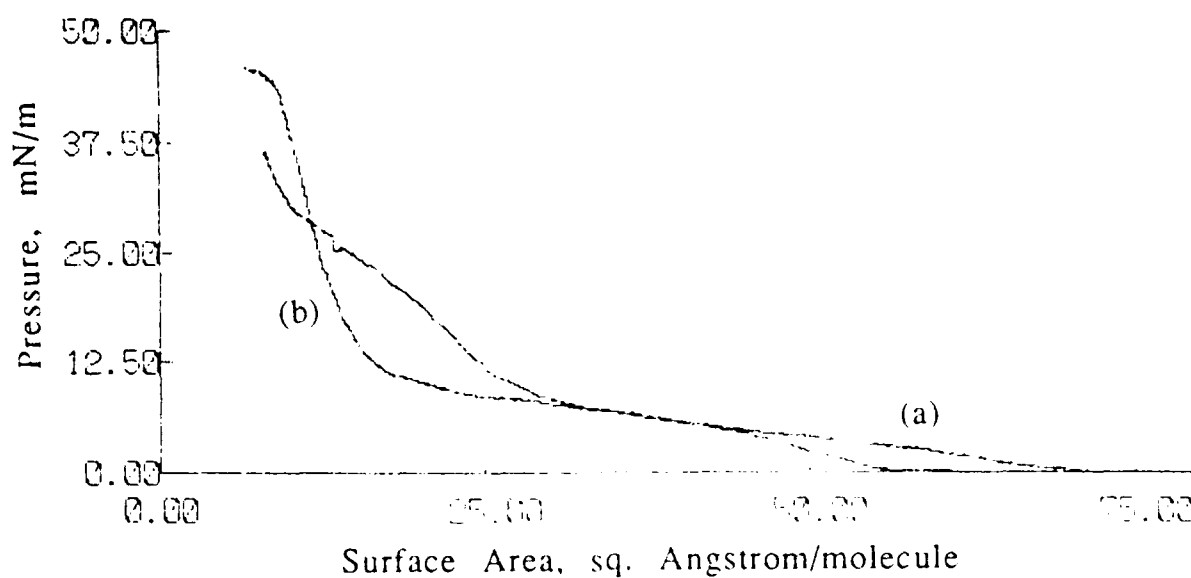Fig.2. Retention of SH properties of copolymer 2 and M5/PMMA with time[8].

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Fig.3. Pressure-area isotherms of PM5C8MA on pure water(a).
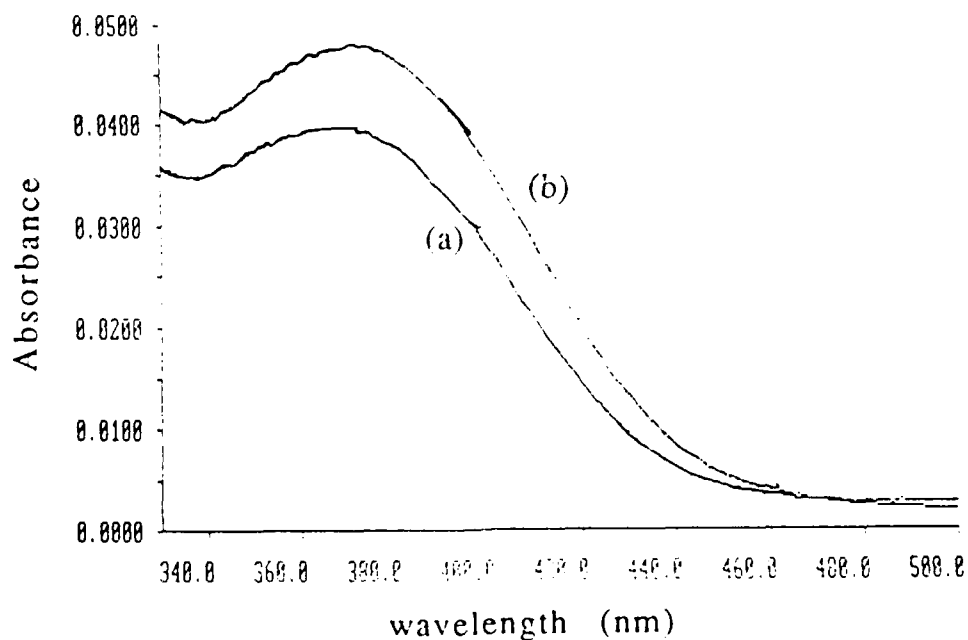Mixture of PM5C8MA and stearic acid (4:1) on $2\times10^{-4}M$ $CdCl_2$ (b).
at 20°C

Fig.4. Polarizad UV-visible spectra of PM5C8MA 11 layers.
p-polarization (a) , s-polarization (b)